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Biological adhesion between bacterial cellulose nanofibrils

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Bacterial cellulose (BC) is sourced naturally in South East Asia from microorganisms such as *Acetobacter xyllinum*, to cater for the multifaceted Asian food industries. It is a renewable, sustainable and biodegradable nanofibril with very high crystallinity, and outstanding properties of stiffness ranging on average, between 78-143GPa[1-3]. Separating the nanofibrils of BC is far simpler and less process-intensive than it is for plant-derived cellulose nanofibrils, making it an attractive 'green nanomaterial' with considerable potential in biomaterials applications. The bulk matter of BC is effectively networked by β-conform hydrogen bonds, which help align cellulose molecules into its tight crystalline structure. Naturally, BC surfaces are also dense with hydrogen bonding sites, however the stiffness of the individual nanofibrils makes it difficult for interfibrilar alignment. BC nanofibrils can therefore create a weak network continuum when packed together with other BC nanofibrils, however the true mechanical potential of BC is never reached in this way. This is reflected in the stiffness of BC sheets, which is reported between 2-15GPa[4,5], and is therefore a factor of ten lower than the nanofibrillar stiffness. How can we scale up BC in a way that reduces losses from its nanofibrillar stiffness? Natural bio-adhesives may have some of the answers…

For materials scientists, the natural world is a constant source of design inspiration. Topics such as structural hierarchy, adhesion, and material morphology are of particular interest, since they elucidate novel design guidelines in the advancement of mechanical materials. Biological adhesion is ubiquitous in the natural world, where it exists in a plethora of different function-specific chemical forms. The design and utility of bio-adhesives in natural materials technologies also constitute an environmentally responsible engineering practice, which for natural materials scientists, should be somewhat of an axiom. Though there are a great many synthetic adhesives that we could use to connect BC nanofibrils, they are often toxic to the environment, and do not easily degrade. This is why, when we find incredible examples of stickiness in the natural world (e.g. aggregate/flagelliform silks, extracellular polymeric substances (EPS) from biofouling diatoms and mussels), we should try to mimic at least their function and design strategies, using similar, naturally sourced bio-adhesives, preferably with minimal chemical modification.

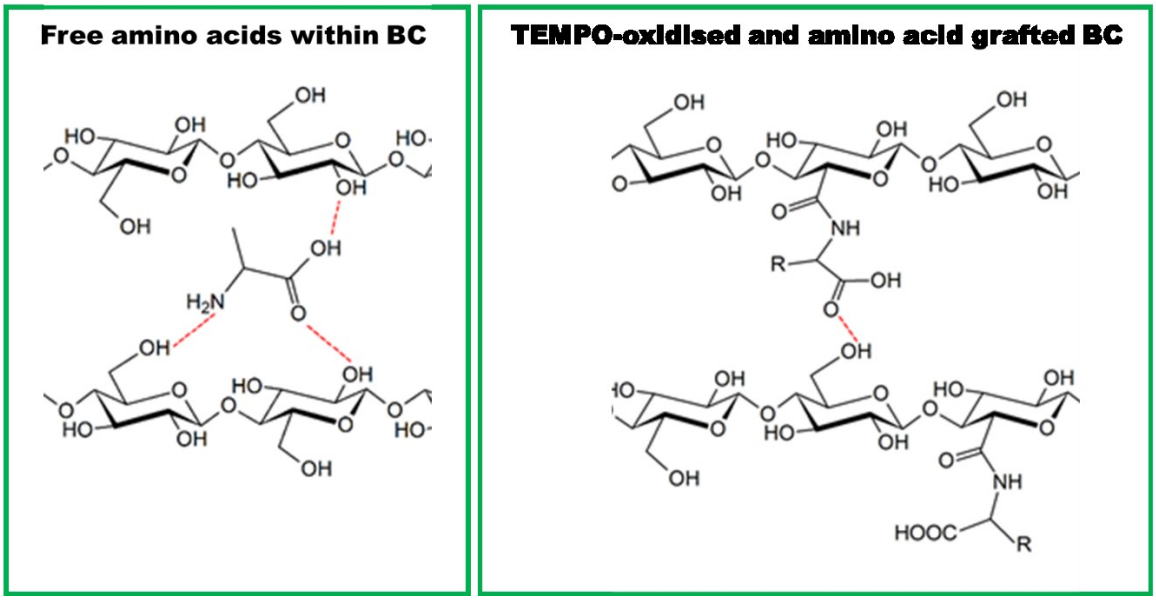
When we consider how bio-adhesives function, we can to a degree, simplify their mechanisms of adhesion to (a) those dominated by intermolecular secondary forces

(electrostatic and van der Waals), and (b) those dominated by off axis sidechains that obstruct intermolecular shear. A good example of (a)can be observed in the nanocrystals of structural biological silks. The stiffness of such nanocrystals is derived primarily from a large concentration of hydrogen bonds that arrange in a quasi-planar manner between β-sheet layers within the nanocrystal. The result is a nanostructure with an exceptionally high stiffness for a polymer[6,7]. Sidechains described in the latter case (b) are different, as secondary interactions that arising between side chains and molecules tend to be off-axis, and therefore less likely to have the same cumulative level of quasi-planar resistance described in (a). In the case of molecules such as chitin, this has been shown to be beneficial to intermolecular adhesion, as the acetyl sidechains laterally stabilise the crystalline form of chitin[8], resulting in both higher stiffness and fracture toughness than in deacetylated chitin (chitosan), which lacks the side chains. Both of the mechanisms of adhesion described (a and b) can significantly improve the mechanical properties of biopolymers. It would stand to reason therefore, that we should be able to improve the properties of 'other' materials by mimicking similar functional designs.

In some of our recent research[4,9], we employed both of the bio-adhesive mechanisms described above to improve the adhesion strength between BC nanofibrils. We applied the specific amino acid monomers; alanine and glycine, as they are known to enable hydrogen bonding dominated 'stickiness' in materials such as silk. In the first instance, we used the amino acids as free-moving secondary bond-forming bio-adhesives between BC nanofibrils. Essentially, during sheet-forming, the amino acid monomers were able to energetically-optimise their locations and orientations between the BC nanofibrils, and in doing so, migrate into the most stable electrostatic attachment. We also grafted the same amino acids to BC surfaces via esterification reaction on TEMPO-oxidised BC nanofibrils. The TEMPO-oxidisation reaction uses 2,2,6,6-tetramethylpiperidine-1-oxyl radicals to oxidise the C6 primary hydroxyl on the cellulose chains to form C6 carboxylate groups. This then allows for the grafting of alanine or glycine as sidechains to the surface of the BC nanofibril. Unlike the free-moving amino acids, when amino acids are grafted to BC surfaces in this way, they are constrained at one end, creating a hairy surface at the molecular-level.

Using experimental tests on manufactured BC sheets (using both methods described above) coupled with molecular dynamics simulations, we learn the following. Free-moving amino acids favour adhering BC surfaces together by aligning themselves parallel with the BC. Amino acids covalently attached to the TEMPO-oxidised BC surfaces on the other hand, are considerably more constrained. The limited mobility in such instances, forces them to electrostatically bond to the nearest available hydrogen-bonding sites (see figure). As such, the mobility of the free amino acid monomers gives them an advantage over pinned sidechains, raising the stiffness of

BC sheets to over 100% that of pure (unglued) BC sheets. We also find that TEMPO-oxidation and amino acid grafting of BC gives rise to moderate improvements in stiffness (ca. 50% improvements). Clearly though, the free movement of bio-adhesives trumps molecular pinned sidechains in this instance, and if we want see BC sheets come closer to their theoretical maximum (nanofibrillar) stiffness, bio-adhesives are a good starting point. Considerably more research needs to be done to tighten that hydrogen bonding network between BC nanofibrils if we are ever to reach their theoretical maximum stiffness. In the future, we will need to apply clever molecular design strategies to bio-adhesive technologies, with the aim of maximising the potential for strong secondary interactions.



References

1. Guhados G, Wan W, Hutter JL (2005) Measurement of the elastic modulus of single bacterial cellulose fibres using atomic force microscopy. Langmuir 21:6642–6646
2. Nishino T, Takano K, Nakamae K (1995) Elastic-modulus of the crystalline regions of cellulose polymorphs. J Polym Sci B – Polym Phys 33:1647–1651
3. Hsieh YC, Yano H, Nogi M, Eichhorn SJ (2008) An estimation of the Young's modulus of bacterial cellulose filaments. Cellulose 15:507–513
4. Pahlevan M, Toivakka M, Alam P (2018) Mechanical properties of TEMPO-oxidised bacterial cellulose-amino acid biomaterials. European Polymer Journal 101:29-36
5. Yamanaka S, Watanabe K, Kitamura N, Iguchi M, Mitsuhashi S, Nishi Y, Uryu M (1989) The structure and mechanical properties of sheets prepared from bacterial cellulose. Journal of Materials Science 24: 3141-3145
6. P.M. Cunniff, S.A. Fossey, M.A. Auerbach, J.W. Song, D.L. Kaplan, W.W. Adams,R.K. Eby, D. Mahoney, D.L. Vezie (1994) Mechanical and thermal properties ofdragline silk from the spider Nephila clavipes, Polym. Adv. Technol. 5 401–410.

7. Sintya E, Alam P (2016) Localised semicrystalline phases of MaSp1 proteins show highsensitivity to overshearing in β-sheet nanocrystals. International Journal of Biological Macromolecules 92:1006-1011
8. Cui, J.; Yu, Z.; Lau, D. Effect of Acetyl Group on Mechanical Properties of Chitin/Chitosan Nanocrystal: A Molecular Dynamics Study. Int. J. Mol. Sci. 2016, 17, 61
9. Pahlevan M, Alam P (2016) Flagelliform silk inspired free amino acid bio-glues in bacterial cellulose biomaterials, Polymer 97: 122–130